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Ortho-Substituent Effects on ^{13}C Chemical Shifts of Some Ortho-Substituted Acetophenone N-Arylimines

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Abstract. Some ortho-substituted acetophenone N-arylimines were synthesized from the appropriate acetophenones and anilines. The products were isolated in the liquid form and were characterized by their ^{1}H and ^{13}C NMR spectra. The results indicate that these imines exist in solution in one isomeric form (The *E*-form). A marked pronounced effect of ^{13}C chemical shifts was observed for the substituted ones compared with unsubstituent imine. Accordingly the ^{13}C substituent chemical shifts (SCS) effects were recorded (Table 1).

Introduction

During the last few years, a very large amount of data concerning the transmission of substituent effect of ^{13}C NMR parameters of imines and some related compounds has become available [1-4]. Many attempts have been made to correlate ^{13}C chemical shifts with the physical properties of molecules, although the Hammett σ parameters are generally accepted as being a useful tool for the investigation and understanding substituent effects on ^{13}C chemical shifts [3].

One particular area of great interest is the study of the effect of substituents on the ^{13}C chemical shifts of aromatic compounds in order to obtain precise chemical shift assignments [4]. The additivity of substituent effects for certain mono substituted benzenoid aromatic compounds on ^{13}C chemical shifts are well characterized in the literature [5]. Aromatic compounds have always had a very important role regarding the investigation of substituent-induced perturbation of σ and π electron distributions this is reflected in chemical and physical properties. ^{13}C substituent chemical shifts (SCS) are useful as a tool to study high shift dispersion, this will result

in obtaining data with ease and a fairly high precision in the probe of ^{13}C chemical shift effect [5].

In extended matter the π electron system is expected to have a long range substituent effect. Correlation between σ constants and ^{13}C-SCS at position considered remote to the substituent in biphenyl chalcones and benzophenones have been investigated for their long range SCS effects [6; 7].

Although considerable research has been carried out on NMR spectra of some imines and their derivatives [8; 9], much work remains to be done to investigate the ^{13}C chemical shifts and the SCS effects of ortho-substituted N-arylimines.

In the present study various ortho-substituted acetophenone N-arylimines (1-10,Table 1) were synthesized from the reaction of the corresponding ortho-substituted aldehydes or ketones with the appropriate aniline. The main objectives are to study the ^{13}C chemical shifts and the SCS effects and to analyze them on the basis of the relative electronic and stereochemical effects of the different substitutents [10; 11] (Table 1).

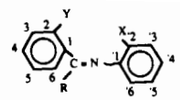
Materials and Method

Preparation of ortho-substituted N-arylimines (1-10), general procedure [12]

Into a 3-necked 250-ml round-bottomed flask attached with a dropping funnel and a magnetic stirrer, the corresponding ortho-substituted methylphenyl ketone (0.1 mol) and the appropriate ortho-substituted amines (0.12 mol) were dissolved in dry benzene (100 ml). Dry nitrogen was passed through the solution by inlet tube for a few minutes while adding simultaneously $TiCl_4$ (0.001 mole) in dry benzene (slight excess of $TiCl_4$ is recommended for good yield) [13] through the dropping funnel dropwisely over a period of half an hour. The whole process was carried out at (0-5°C). After completing the addition, the source of cooling was removed and stirring was continued for another two hours at room-temperature. Then the reaction mixture was refluxed for about three hours. It was then cooled to room-temperature, filtered and the solvent in the filtrate was distilled under vacuum. The residue thus obtained was distilled under vacuums. The physical properties and ^1H NMR data of the prepared compounds were depicted in Table 2.

The NMR spectra were obtained on a Jeol JNM FX-100 spectrometer, operating at 25 MHz and with a 10 mm ^1H /^{13}C dual probe. Computation was made using JC 980B computer with 16K memory. The deuterium resonance of the solvent was used for internal lock; data were collected over a 5000Hz sweep width using 8K data points; proton noise decoupling and with 10 μs pulse width (45°) repeated at 25 s

Table 1. ^{13}C NMR chemical shifts data of N-arylimines 1-10 in $CDCl_3$ at 28°C



Compound	Y	X	R	δR	δC=N	δC-1	δC-2	δC-3	δC-4	δC-5	δC-6	δC′-1	δC′-2	δC′-3	δC′-4	δC′-5	δC′-6	δY	δX
1	H	H	H	-	161.40	137.40 (-)	130.2 (-)	129.70 (-)	132.40 (-)	129.70 (0.50)	130.20 (0.40)	153.20 (0.10)	122.0 (-)	129.80 (-)	127.0 (3.80)	129.80 (7.80)	122.0 (-7.8)		
2	H	H	CH_3	17.50	165.3	139.6 (-)	127.3 (-)	128.4 (-)	130.50 (-)	129.0 (1.70)	127.30 (-1.10)	151.90 (-)	119.40 (-)	127.30 (-1.10)	123.20 (1)	128.40 (9)	119.40 (-9)		
3	H	NO_2	CH_3	29.41	161.17	138.52 (10.02)	131.98 (3.38)	129.98 (0.83)	125.64 (-2.86)	131.98 (3.46)	129.33 (0.83)	137.50 (9.50)	131.45 (-7.85)	129.35 (5.85)	131.54 (8.41)	131.45 (5.95)	129.35 (-5.95)		
4	CH_3	CH_3	CH_3	29.47	165.56	138.32 (-1.96)	131.39 (-5.13)	129.28 (0.22)	125.57 (-4.82)	131.39 (6.79)	129.28 (0.22)	137.55 (-15.01)	131.92 (3.66)	129.28 (0.22)	125.57 (3.48)	131.92 (15.56)	129.28 (0.22)	21.45	21.54
5	CH_3	Cl	CH_3	29.53	162.89	140.0 (0.26)	135.15 (-1.37)	129.86 (0.80)	127.54 (-2.85)	131.04 (6.44)	129.86 (0.8)	140.84 (41.46)	131.45 (5.75)	129.28 (0.48)	131.98 (8.28)	131.45 (14.15)	129.28 (0.48)	21.89	
6	CH_3	Br	CH_3	29.47	162.55	138.34 (-1.92)	131.39 (-5.13)	129.28 (0.22)	125.57 (-4.82)	131.39 (6.79)	129.28 (0.22)	137.55 (-17.55)	131.98 (18.38)	128.22 (-3.38)	131.98 (7.59)	131.39 (14.18)	128.22 (-3.38)	21.54	
7	NO_2	CH_3	CH_3	30.00	165.05	145.72 (11.22)	130.74 (-16.46)	127.34 (3.84)	124.23 (-7.17)	130.74 (-2.66)	127.34 (3.84)	137.55 (15.01)	134.21 (5.61)	127.35 (-1.17)	130.75 (8.66)	134.21 (17.85)	127.35 (-1.17)		21.56
8	NO_2	Br	CH_3	30.11	163.12	145.65 (11.15)	132.80 (-14.4)	129.75 (6.25)	127.23 (-4.17)	130.63 (-2.77)	129.75 (6.25)	137.79 (17.31)	134.15 (20.55)	128.23 (-3.37)	132.27 (8.47)	134.03 (16.23)	128.23 (-3.37)		
9	NO_2	Cl	CH_3	30.05	163.27	145.71 (11.12)	134.26 (12.94)	127.32 (3.82)	124.34 (-7.06)	130.75 (-2.65)	127.32 (3.82)	137.65 (-14.65)	134.01 (8.31)	128.0 (-0.8)	130.76 (7.06)	134.0 (16.7)	128.23 (-0.57)		
10	NO_2	NO_2	CH_3	30.00	154.0	145.72 (11.58)	135.62 (11.58)	129.75 (6.25)	127.3 (-4.10)	130.76 (-2.64)	129.75 (6.25)	137.56 (-9.44)	134.21 (-5.09)	125.82 (2.32)	130.75 (7.65)	134.21 (8.71)	125.82 (2.32)		

1) open data are relative to chemical shifts in ppm.

2) values in parentheses relative to SCS effect in ppm.

3) (+) shielding (-) deshielding

Table 2. Physical properties and proton chemical shifts (δ) of substituted acetophenone anils in $CDCl_3$ at 28°C

Compound No.	Y	X	R	B.P. °C	C-CH_3	Aromatic	Others
3	H	NO_2	CH_3	312	2.54	7.28–7.70	–
4	CH_3	CH_3	CH_3	345	2.53	7.30–7.72	2.57[a]
5	CH_3	Cl	CH_3	308	2.12	7.01–7.72	2.56[a]
6	CH_3	Br	CH_3	355	2.52	7.20–7.33	2.56[a]
7	NO_2	CH_3	CH_3	348	2.56	7.42–8.14	2.56[a]
8	NO_2	Br	CH_3	310	2.56	7.49–8.10	–
9	NO_2	Br	CH_3	311	2.34	7.45–8.12	–
10	NO_2	NO_2	CH_3	360	2.57	7.26–8.09	–

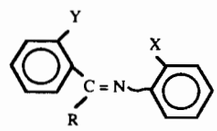
a) CH_3 attached to the N-aryl and C-aryl ring (two overlapped singlets).

b) CH_3 attached to the C-aryl ring (singlet)

intervals. The ^{13}C chemical shifts were reproducible within the effective computer digital solution of 0.05 ppm. All the spectra were recorded at 28°C and the sample concentration was 0.5 M using TMS as internal standard.

Results

All the investigated imines (1-10, Table 1) were prepared and characterized by their ^1H and ^{13}C NMR spectra.



	Y	X	R
1.	H	H	H
2.	H	H	CH_3
3.	H	NO_2	CH_3
4.	CH_3	CH_3	CH_3
5.	CH_3	Cl	CH_3
6.	CH_3	Br	CH_3
7.	NO_2	CH_3	CH_3
8.	NO_2	Br	CH_3
9.	NO_2	Cl	CH_3
10.	NO_2	NO_2	CH_3

Discussion

The imines under the study were found to exist in solution in one isomeric form (the *E*-form) [14]. The results listed in Table 1 indicates a marked pronounced effects of ^{13}C chemical shift of C-1; C-2; C-4 as well as C′-1 and C′-2 in comparison to the unsubstituted N-arylimine, which indicate not only the influence of inductive effect, but also due to the changes in the size and electronic structures of the ortho-substituents at both positions (Y and X) in the imines (1-10) [4]. Accordingly the ^{13}C chemical shifts C-1 and C-2 for the unsubstituted imine (1, Table 1) were found to be at δ 137.4 and δ 130.2 while those for the C′-1 and C′-2 were at 153.2 and 122.0 ppm respectively. Similarly the chemical shifts for the substituted imine (10, Table 1) were recorded at δ 145.72 and δ 135.62 for C-1 and C-2 whereas those for C′-1and C′-2 were observed at δ 137.56 and δ 134.21. Considering the recent reports [3; 15] which suggested that, there was an obvious ^{13}C chemical shifts effect in a different way on meta and para substitutent and it was interesting to note that the correlation holds over the combination of the substituent at both positions [2]. Based on that finding there is an obvious variations between C-1 and C-2 shifts as well as C′-1 and C′-2of the substituted N-arylimines (3-10,) when compared to the unsubstituted imines (1 and 2) particularly in the electron withdrawing substituent groups like (10,9,8,7, Table 1). The marked effect of variation in the chemical shifts of C-1 and C-2 with and C′-1 and C′-2in imines (3-10, Table 1) may be attributed to the influence of a large inductive and resonance effects of the substituents on the electronic environment of the substituent carbon nuclei [4].

All the SCS values for imines (1-10, Table 1) were calculated using the parameter for liquids in which external TMS use, the arbitrary value of δ 128.5 of benzene was commonly applied in SCS calculation (Table 1) [15]. The SCS effect of the different substituents (X and Y) at the positions of the title compounds (3-10) were obtained similar to the method mentioned in [16] with the following specifications:

$$\delta SCS = \delta(\text{parent imine 1 or 2}) - \delta(\text{substituted imines 3-10, Table 1}).$$

There is an effect of shielding observed on the C-1 and C-2 as well as C′-1 and C′-2 on the aryl carbons of the prepared imines (3-10, Table 1) in relative to the aryl carbons of the parent unsubstituted imines (1 and 2) which are markedly affected by SCS on both C=N as well as with ortho-substituents in imines (3-10,). Accordingly the additivity of chemical shifts in imines (3-10, Table 1) were used to check the assignment on C-1 to C-6 as well as C′-1 to C′-6 of the prepared imines using SCS values tabulated in the literature [5] using $CDCl_3$ solution.

The results in Table 1 show that SCS effect of C-1 to C-6 in imines (3-6) where the substituents are electron donating groups were found to be rather small in comparison to that of unsubstituted imines (1 and 2). But there is apparent long range

effect with significant variation at C′-1, C′-2, C′-4 and C′-5 in the same imines which could be attributed to the substituent effects of electron withdrawing groups as well as to the substituent inductive (polar) field effect [17]. The SCS observed for the distant carbon atoms would not only show the geometric dependence indicative of electrostatic polarization but would also show a dependence on the nature of the whole system [15; 17]. On the contrary there is marked pronounced SCS effect on C-1 to C-6 as well as C′-1 to C′-6 imines (7-10, Table 1) where all the substituents are electron withdrawing groups except in imine 7 Table 1, where X is electron donating group. The SCS effect could be assumed to be due to purely magnetic effects operating on the substituent with strong anisotropic bonds which may give rise to differential shifts at ring carbon most importantly at the C-1 and C′-1 positions. Moreover, the SCS effects may also be attributed to substituent induced changes in electron density which not only linearly related but also related to the factor of electronic state of molecules [5]. The observed SCS effects may also possibly be due to the changes in electronic densities in the framework of the system of the aryl ring [5; 6].

The resonance of the imino carbon $^{13}C{=}N$ was found to have an obvious effect of increasing steric demand of the ortho substituents, this resulted in decreasing the influence of the phenyl group (*i.e.* its electron density enhancement) [18] since such changes of the aryl ring directly influence on the imino groups [9]. The imines with electron withdrawing substituents (Table 1) have significantly high field shifted imino carbon resonance C=N as a result of changing polarization [19]. There is evidence for substituent effect (electronic as well as steric interaction) between the N-aryl group and the neighboring substituent groups since this polarization considerably destabilized the dipolar tranisition state forcing the ring to twist out of the C=N plane and thus making the variations in the $^{13}C{=}N$ positions of the different substituent groups (3-10, Table 1) [18].

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تأثير البدل في الموضع أورثو على مواقع خطوط طيف الكربون ـ١٣ لبعض الإيمينات العطريّة المشتقة من أورثو ـ أسيتوفينون

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(استلم في ١٤١٣/١٢/٣٠هـ؛ قبل للنشر في ١٤١٤/١١/١٣هـ)

ملخص البحث. تمّ تحضير عدد من مركبات N- أريل أيمين أسيتوفينون الحاوية على بديل في الموضع أورثو ومن ثم أجريت دراسة مفصّلة لأطياف الرنين النووي المغناطيسي لتحديد مواضع خطوط الطيف للكربون ـ١٣ وأثر البدل المختلفة في تغيير هذه المواضع. ولقد ركّزت الدراسة على فحص التأثيرات الإلكترونية والتأثيرات الفراغية للبدل المختلفة. وحساب تأثير البدل على قيمة (SCS) ودلّت النتائج على وجود تأثيرات واضحة لهذه البدل نتيجة للتغيرات التي تحدث على السحابة الإلكترونية للحلقة إضافة إلى التأثيرات الفراغية والإلكترونية المختلفة.